ESA based in-fiber nanocavity for hydrogen peroxide detection

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***Abstract*— A fiber-optic sensor sensitive to hydrogen peroxide has been designed based on the electrostatic layer-by-layer self-assembly method. Prussian Blue has been deposited in a polymeric structure formed by poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA). The concentrations that can be detected range between 10^{-6} and 10^{-3} M, and recovery of the sensor after immersion into reductive agent has been proved successful. The response of the sensor is independent of the pH for values that range between 4 and 7.4. Some rules for estimation of the refractive index of the material deposited and the thickness of bilayers are also given.**

***Index Terms*—Electrostatic self-assembly, hydrogen peroxide, optical fiber sensor, nano-structures.**

I. INTRODUCTION

Nanotechnology is becoming a revolution in many fields such as photonics, biotechnology, electronics, materials, information and telecommunications, just to mention a few [1-4]. The key point is to join many disciplines to control the creation of nanostructures used for many applications. For this reason it has been considered as the science of the 21th century. If we focus on the field of sensors, determination of hydrogen peroxide (H_2O_2) concentration is of great importance in many fields. It is the chemical product of reactions catalyzed by a large number of oxidase enzymes, consequently it has application in food, pharmaceutical, clinical and environmental analysis. In these fields low concentrations are to be detected, which makes necessary more sophisticated sensor devices for this purpose. In addition to this, hydrogen peroxide is used in many industrial processes as an oxidizing, bleaching and sterilizing agent. It is also the waste product in industries like atomic power stations. In these last cases higher concentrations of hydrogen peroxide are present and simpler sensors can be used.

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In this paper we will present a fiber-optic sensor for detection of low concentrations of hydrogen peroxide, which is adequate for biological purposes. Other advantages are also explained such as its small size, low cost and easiness to handle. It is based on the Electrostatic Self Assembled (ESA) monolayer process, which is a nanotechnology explained in section II.

There is a large number of techniques for detection of H_2O_2 in the literature. Titration is more commonly used for calculating the concentration of hydrogen peroxide of a sample solution with a reagent such as potassium permanganate [5]. However, in order to determine micro and submicromolar levels other alternatives are necessary. The two main groups are electrochemical detection [6-12], and spectroscopy [13-23]. Among these, spectroscopy has been selected because it avoids the application of voltage, what is advantageous for medicine applications, and because it is easy to handle. Spectroscopy methods can also be subdivided into chemiluminescence [13-14], spectrofluorometry [15-17] and spectrophotometry [18-23]. This last one consists of the oxidation of a chromogenic hydrogen donor with hydrogen peroxide leading to its oxidized form, whose absorbance changes. This effect has been studied in Prussian Blue by other authors [22,23], where no enzyme is needed for accelerating the reaction. This effect has been proved successful in this sensor and changes in the absorbance are important in a wide range of wavelengths at least between 650 and 1000 nm; including the first optical communications window.

Regarding the deposition technique, the construction of a nanostructure at the end of a fiber pigtail by using electrostatic layer-by-layer (LBL) self-assembly method has been selected. This method has been proved successful in the fabrication of sensors in many other substrates [8,10,15,18]. In this case fiber-optic has been selected for the substrate, which shows fine properties such as immunity against electromagnetic interferences, possibility of multiplexing of sensors and small size. Other hydrogen peroxide sensors are based on carbon paste deposition or sol-gel technique [6,10,11,13,14,17,19]. However, they lack the advantages of the nanotechnique presented in this work. The nanostructure deposited at the end of fiber optic is formed by electrostatic attraction, consequently it is more stable. In addition to this, a variety of polymer structures, where the redox indicator is introduced, can be selected. This should permit the immunity of the sensor

against cross-sensitivity caused by other molecular species. Furthermore, the small thickness of the nanocavity formed allows to use a simple LED as a light source for the circuit of detection, which saves costs. The construction of layers with this method also should permit a new measuring technique not based on a change of the signal level, which is dependent on the pH, but on the slope of the change produced in the signal.

The concentrations that can be monitored by the LBL structure range from 10^{-6} to 10^{-3} M of H_2O_2. Prussian Blue serves as the redox indicator and causes a change in the absorbance. The sensor is recovered after immersion in a reductive agent such as ascorbic acid [22,23]. Depending on the slope of the change in the absorbance of the sensor after introduction of hydrogen peroxide, it will correspond with higher or lower concentrations. And a wide range of pHs have been proved between 4 and 7.4, demonstrating that the response of the sensor is independent of the pH.

The remainder of this paper is organized as follows. In section II the electrostatic LBL self-assembly method and its main applications is explained. Later on, in section III the experimental elements are detailed. In section IV the sensing mechanism is analyzed by comparing the construction of the bilayers at the end of the fiber with the results obtained with a simulation program based on Rigorous Coupled Wave Analysis method. In section V there is an analysis of results obtained. Finally, concluding remarks are given in section VI.

II. The Electrostatic Self-Assembled Monolayer Process

The Electrostatic Self-Assembled (ESA) monolayer process is a technique used to build up coatings on a variety of different substrate materials such as ceramics, metals, and polymers of different shapes and forms, including planar substrates, prisms, and convex and concave lenses. In this work it is shown the applicability to a fiber optic substrate for the aim of creating a fiber-optic H_2O_2 sensor.

This method is based on the construction of molecular multilayers by the electrostatic attraction between oppositely charged polyelectrolytes in each monolayer deposited, and involves several steps [24]. The ESA film deposition method is described schematically in Fig. 1.

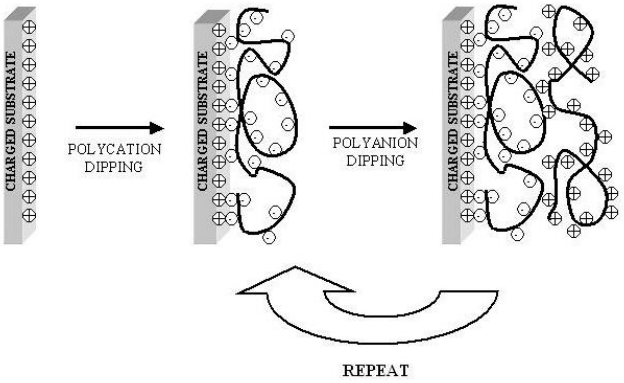


Fig. 1. Schematic of ESA deposition process.

First, a substrate (in this case the optical fiber) is cleaned and treated to create a charged surface. Then, the substrate is exposed to a solution of a polyion of opposite charge for a short time (minutes) and by adsorption a monolayer of polyions is formed on the surface. In this way, the substrate is alternately dipped into solutions of cationic and anionic polymers (or appropriately charged inorganic clusters) to create a multilayer thin film, a polyanion-polycation multilayer. After each monolayer is formed we rinse the sample in pure water to remove the excess of molecules that are not bound and that do not contribute to the monolayer structure.

The molecular species of the cationic and anionic components and the long-range physical order of the layers determine the resulting coating properties. It is important to notice that the polyanions and polycations overlap each other at the molecular level and this produces an optically homogeneous material [24]. The individual layer composition and thickness can be controlled and substrates may include metals, plastics, ceramics and semiconductors.

The versatility of ESA method for the synthesis of materials, permits the application of this technique to design or fabrication of different optical fiber devices such as nanoFabry-Perot interferometers [25], fiber optic gratings [26], or photonic bandgap structures [27]. The same type of structures could be used to develop optical fiber sensors [15,28]. One idea that will be explained in section III is to include a chromogenic or fluorometric substance in one of the polyelectrolyte solutions whose absorbance changes in the presence of the analyte it is desired to detect.

III. Experimental

A. Instrumentation

Power measurements were obtained using a reflection scheme where the light source is a Hewlett-Packard 9537 HFBR 1424 LED at 810 nm and a Ophir LaserStar photodetector detects the reflected power measurements at the first optical communications window. The pH of the different solutions was adjusted with a pHmeter GLP22 of Crison.

B. Assembly of multilayer films

The materials used for deposition of cationic and anionic layers are poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) respectively. The method used for including Prussian Blue into the polymeric structure is premixing with the polycation [18]. In this method the dye is mixed with a polyion with the opposite charge. Both of them will associate with the other oppositely charged polyion, leading to the construction of the structure. Some experiments where performed with conjugation technique. Prussian blue was mixed with PAA and the material was deposited, but changes in the signal were not as clear as with premixing. The concentration of PAH is 2 g/L, PAA 5 ml/100ml whereas Prussian Blue concentration is 2.5 g/L. Annealing after concluding the construction of the LBL structure at the end of

the fiber pigtail is another important parameter with consequences in the performance of the sensor. It has been proved that sensors must stay at 100 ºC during at least two hours for a stable performance. Otherwise there is a continuous destruction of the films when immersed in buffer solutions at different pHs.

C. *Materials*

The polycation (PAH), M_w 70000, and the polyanion (PAA), M_w 30000, were obtained from Aldrich. Prussian blue, was obtained from Riedel-de Haën AG. And ascorbic acid, was obtained from Panreac Acetic and phosphate buffer solution of 25 mM of ionic strength were fabricated in our laboratory. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH of the polymers and Prussian Blue solutions. All water was filtered through a Milipore Q plus 185 purification system.

IV. Sensing Mechanism

In this section an analysis of the construction of the sensor is given. As more and more bilayers of PAH+Prussian Blue /PAA are added at the end of the fiber, the reflected power obtained in the setup represented in Fig. 2 changes. A nano Fabry-Perot cavity is formed between the fiber and air, and the modification of its thickness as the material is deposited causes a sinus plot whose amplitude decreases due to the absorbance [21].

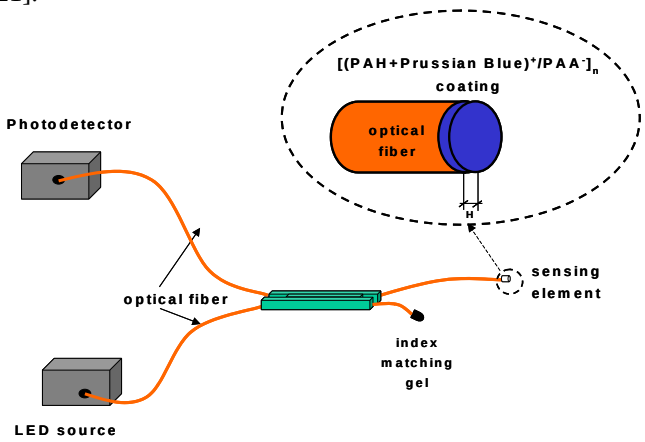
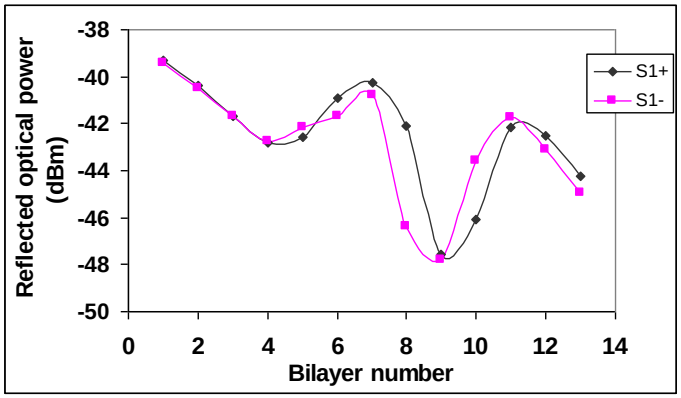
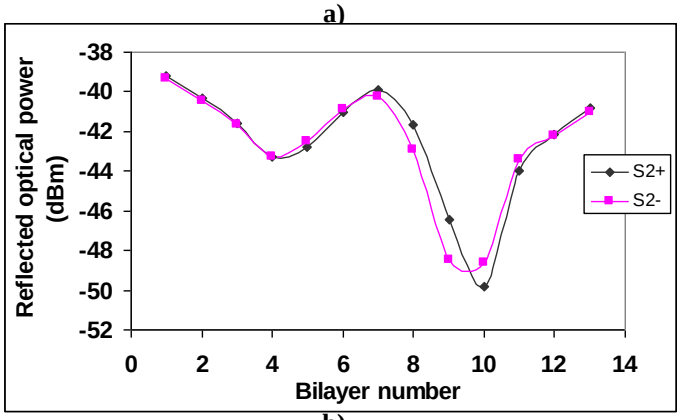


Fig. 2. Experimental setup to detect the power reflected by the nano Fabry-Perot cavity.

In Fig. 3 the reflected power change produced by the deposition of the LBL structure at the end of two fiber pigtails is shown. The sensors have been constructed in parallel by introducing them in the same positive and negative solution. The plots are quite similar but they are not the same. From these plots the refractive index and the thickness of bilayers can be estimated by comparing it with a theoretical plot obtained with a program developed based on the Rigorous Coupled Wave Analysis method [29].



a)



b)

Fig. 3. Experimentally reflected optical power in two sensors constructed in parallel as a function of the number of bilayers deposited. Both positive (+) and negative (-) polyion plots are represented.

First of all, it is important to note whether the refractive index of the material deposited at the end of the fiber presents a refractive index higher or lower than that of the fiber. If it is lower than that of the fiber the shape of the plot will be that of Fig. 3. Otherwise there will be a relative π shift in the construction curve originated. In [30] it is proved that there is a π rad phase shift in the reflected optical beam, if the refractive index of the fiber is lower than that of the material deposited at the end. This displacement is not present in the other case, which causes the relative shift between plots obtained in both cases considered. This effect is visualized in Fig. 4, where there is a π shift between the plots obtained for refractive indexes higher than that of the fiber (1.8 corresponding to $[Au:PDDA^+/PSS^-]_n$ and 2.458 corresponding to ZnSe), and refractive indexes lower than that of fiber (1.33 (similar to water) and 1.37 of $[PAH+Prussian\ Blue^+/PAA^-]$).

As the contrast of indexes between fiber and deposited material increases, the period is shorter and the amplitude is higher. Both parameters define the refractive index of the material deposited. However, the period in nanometers cannot be directly deduced with experimental plots. Consequently, of the two experimental parameters, we will focus on the amplitude to obtain in first place the refractive index. As the index of refraction contrast with fiber is higher, the amplitude increases, which agrees with bandgap and Fabry-Perot cavities theory.

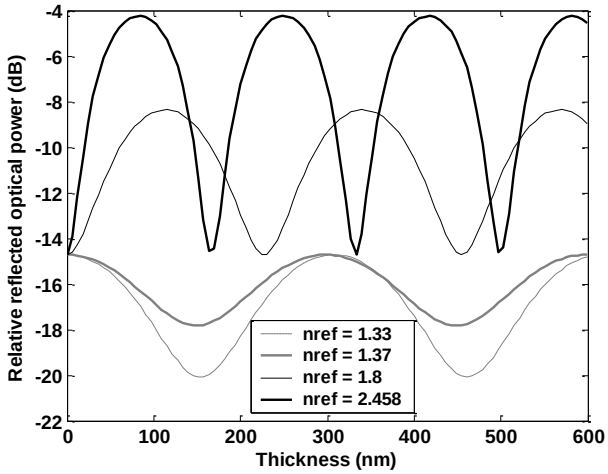


Fig. 4. Relative reflected optical power as a function of the thickness of the nano Fabry-Perot cavity for four different refractive indexes.

Once the refractive index is estimated, the thickness of bilayers is approximated by using this formula:

$$\phi = \frac{4 n_2 d \pi}{\lambda} \qquad (1)$$

where ϕ is the phase shift of the optical beam in the cavity formed by the coating with length d, n_2 is the refractive index of the coating and λ is the wavelength of the LED.

In the simulation of the construction curve of the sensor of Fig. 3, losses caused by absorption have been taken into account and the plot adjusts except at the beginning, where it is well known that the growth of bilayers is slower and not uniform at the first bilayers. Consequently starting from the fourth bilayer both plots coincide.

The value obtained is 1.370+0.074i. In this case both theoretical and experimental plots (see Fig. 5) only differ in the first bilayers where the growth is slower. Normal growth is achieved at fourth layer. The thickness obtained theoretically with expression (1) taking the real part is 59.12 nm, which is almost exactly the experimental value obtained by fitting the experimental plot with the theoretical one: 59.8 nm.

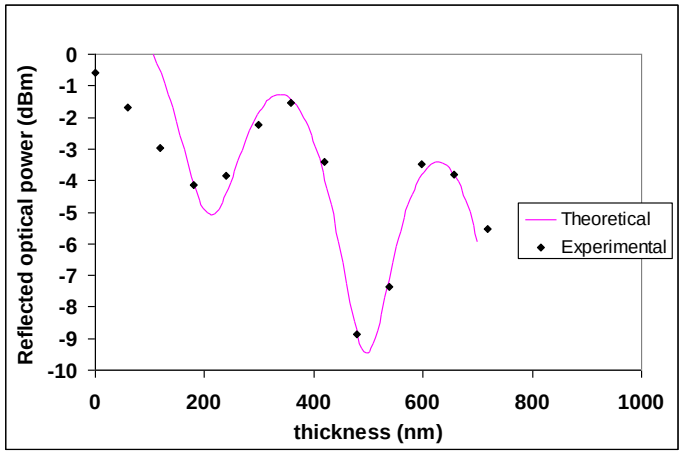


Fig. 5. Reflected optical power as a function of the thickness of the material deposited at the end of the fiber theoretically and experimentally.

V. Results and Discussion

The selection of Prussian Blue in combination with a PAH/PAA LBL structure obeys to two factors. Prussian Blue shows fine properties like its solubility in contrast to bromopyrogallol red for instance, and its usage in the literature as a redox indicator for the detection of H_2O_2 in electrochemical sensors [7,12] and spectroscopy [22,23]. In these last two references, it is asserted that Prussian Blue shows a maximum in absorbance located at 720 nm, consequently measures should be taken around this wavelength. However, this redox indicator is deposited in a matrix of *N*-substituted polypyrrole. And it has been proved in [17] that the maximum in absorbance of a redox indicator can be shifted in a great manner if it is immersed in a matrix of other material. As a result we have obtained the absorbance spectrum of Prussian Blue immobilized in our PAH/PAA LBL structure before and after oxidation with a high concentration of hydrogen peroxide. This is represented in Fig. 6, where changes occur at a range of wavelengths between 600 and 1000 nm. The experimental setup used to obtain this plot is the same represented in Fig. 2 with the exception that a white light source replaces the LED and a spectrometer is used instead of the photodetector. The first optical communications window is located in this range, consequently an LED source at 810 nm and a photodetector at this first window have been selected for the purpose of saving costs even though the maximum is located at 720 nm. In this case there has been no shift of absorbance spectrum due to the polymer structure.

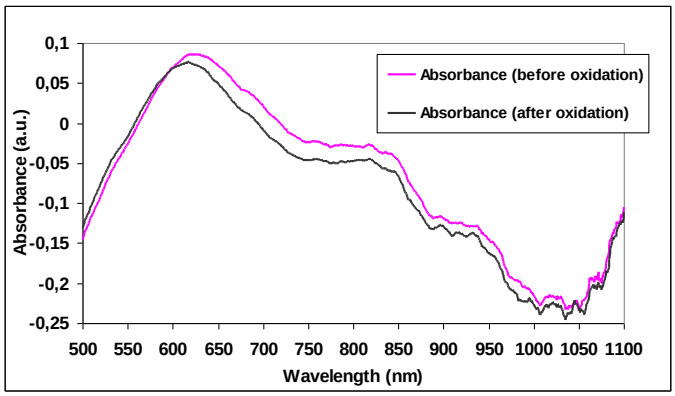


Fig. 6. Absorbance before and after oxidation of PAH+PB/PAA structure with H_2O_2.

The first sensor analyzed consists of a PAH+PB/PAA structure constructed with the concentrations detailed in section III. 17 bilayers have been deposited, and a thermal treatment was performed during 2 hours at 100 degrees to avoid progressive desorption of bilayers. However, sensitivity is an important parameter that reduces if higher thermal treatment is performed, consequently a trade off must be maintained between sensitivity and robustness. Both factors cannot be improved at the same time. In Figs. 7 and 8 the response of the sensor at a pH of 4 for different concentrations of H_2O_2 is analyzed. These measures have been taken one

week after its fabrication when the sensor has stabilized its sensitivity. The concentrations that can be detected range between 5 μM and 1 mM. First of all, Prussian Blue is reduced with reductive agent such as ascorbic acid. After this, we introduce the sensor in a buffer solution, and the injection of H_2O_2 provokes a change in the reflected optical power whose slope and response time depends on the concentration of H_2O_2 introduced. In Fig. 7 some responses to different concentrations are given. The levels of signal under the presence ascorbic acid and H_2O_2 maintain throughout the time, which means that the structure is stable after reduction and oxidation steps. It is easy to appreciate that as higher concentration is introduced: 5·10-6, 5·10-5, 2·10-5, 10-5, 2·10-4, and 5·10-4; the response time and slope of the change produced in the signal decrease and increase respectively. To analyze this fact, in Fig. 8 the response time and the slope of the changes is represented as a function of the concentration. The important conclusion obtained is that there is a linear dependence between the concentration of H_2O_2 and the slope of the change produced in the reflected power. Later it will be proved that this parameter is independent of the pH of the solution where the sensor is immersed.

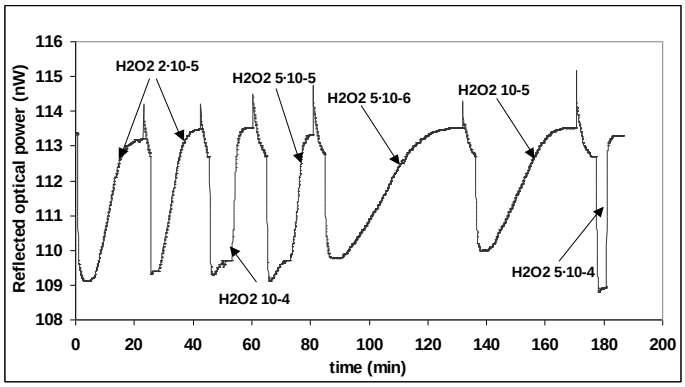


Fig. 7. Reflected power for different concentrations of hydrogen peroxide at a constant pH 4.

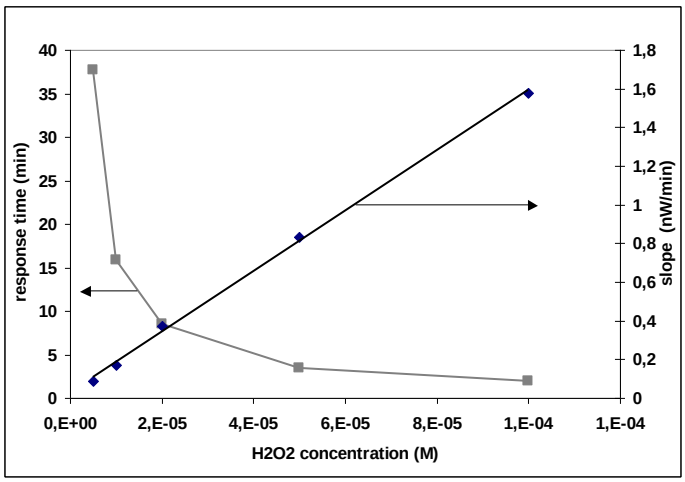


Fig. 8. Response time and slope of the change in the reflected power for different concentrations of hydrogen peroxide at a constant pH 4.

In Fig. 8 the plot for the slope of the change produced in the reflected power for different concentrations of H_2O_2 coincides with a linear tendency line. In Fig. 9 we analyze the response of another sensor with the same characteristics as the first sensor except that it has been cured at 150 ºC. It has been measured at pH 7.4, which is the normal blood pH. The concentrations that have been introduced are 5·10-6, 2·10-5, 2·10-4, 5·10-4, and 10-3. The sensitivity is much higher because stabilization has not been reached. It was measured three days after its construction. The level of the signal is maintained like in the first sensor. And again in Fig. 10 the slope of the change in the reflected power for different concentrations is linear. Response times are also given.

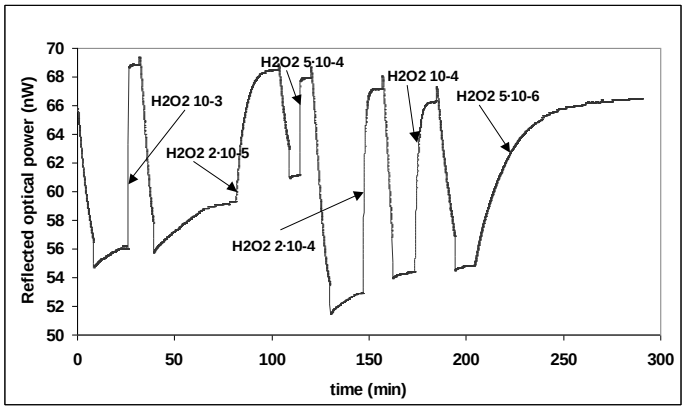


Fig. 9. Reflected power for different concentrations of hydrogen peroxide at a constant pH 7.4.

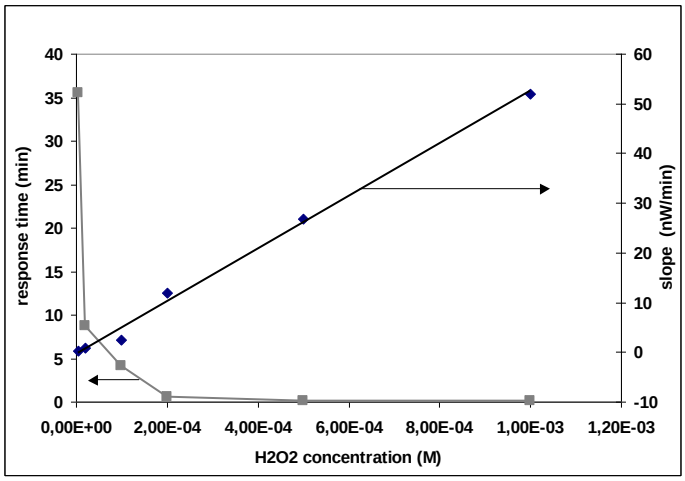


Fig. 10. Response time and slope of the change in the reflected power for different concentrations of hydrogen peroxide at a constant pH 7.4.

After these two examples of analysis of the response of two different sensors for different pHs, the response of the first sensor for three different pHs has been analyzed in Fig. 11. The response time is different depending on the pH, but the slope is independent of the pH, which permits the detection of different concentrations of H_2O_2 without the need of a calibration simple electronic circuit. This is a great advantage in comparison with most of the sensors in the literature that present the drawback of showing different response for different pHs. The measures have been taken 19 days after the construction of the sensor and the concentrations analyzed are 10^{-3}, 10^{-5} M, showing the sensor no problem if the order of

introduction of these two concentrations changed. Furthermore, the problem of maintaining the signal level after some measuring disappears because the slope is independent of this factor.

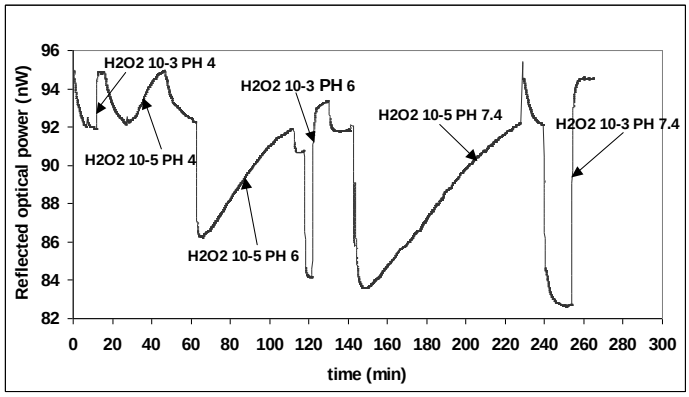


Fig. 11. Reflected power for different concentrations of hydrogen peroxide at a pH 4, 6 and 7.4.

It was checked that the sensor could be stored during 40 days in air without significant lost of its detection capacity. Storing in distilled water causes progressive desorption of layers consequently it is not advisable to leave the sensor in that medium during more than two days. In 12 hours it loses one bilayer.

About reproducibility it has been proved that the sensor can detect H_2O_2 concentrations after immersion in a reductive agent such as ascorbic acid during at least 40 days. During the first 6 days the sensor is more unstable and there is a faster lost of sensitivity. After that, there is an stabilization and the range of concentrations that can be detected is located between 10^{-5} and 10^{-3} M. The sense for using buffer solutions and introducing different concentrations of H_2O_2 is to avoid variations of pH that can interfere. However, it has been proved that the slope of the change produced in the reflected power by introduction of H_2O_2 is independent of the pH at least in the range between 4 and 7.4. Consequently this sensor can measure concentrations in non-buffered solutions.

Finally, the optical cross-sensitivity of the sensor to reductants and other well known elements that can interfere with an H_2O_2 sensor has been analyzed. 2.5 mM concentrations of chloride, bromide, iodide, oxalate, thiocyanate, tartrate, urea, sulfate, phosphate and glucose were analyzed and no changes were appreciated. Only arsenite produced a slight change of the signal but not in the state of Prussian Blue, because the sensor recovered its signal after immersion in another solution without the need of an oxidizing or reducing agent.

VI. Conclusion

In this work a new fiber-optic hydrogen peroxide sensor has been designed applying the electrostatic LBL self-assembly method. An analysis of the construction curves is given where both the refractive index of the material deposited and the thickness of the bilayers can be estimated. This avoids the need of other techniques like the use of an ellipsometer. Premixing of Prussian blue with the polycation permits to detect different concentrations of H_2O_2 that range 10^{-6} and 10^{-3} M. For higher values the sensor saturates. Recovery of oxidized Prussian Blue has been proved successfully after immersion in a reductive agent such as ascorbic acid. The reflected power depends on the pH, but the slope of the change in the reflected power produced by different concentrations of H_2O_2 is independent of the pH in the range between 4 and 7.4, consequently no buffer solution is needed for measuring. In addition to this, the sensor is immune to interferences of a large number of products except for ascorbic acid, which is the reductive agent of our sensor. To our knowledge this is the first time the electrostatic LBL self-assembly method has been applied to the design of an H_2O_2 sensor, where detection of the concentration is based on the slope of the change of signal produced by oxidation of Prussian Blue. This avoids problems produced by changes in signal levels in sensor measuring. This sensor presents important applications in food, clinical and pharmaceutical analysis and its possible utilization in industry. Furthermore it could be used in a double-channel flow injection analysis (FIA) system as it has been done in other sensors [23].

VII. Acknowledgment

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